DIRECTIONAL SOLIDIFICATION OF MULTICOMPONENT SUPERCONDUCTING SYSTEMS UNDER ZERO G CONDITIONS

J. T. A. Pollock* and Fritz Wald

TYCO LABORATORIES, INCORPORATED
WALTHAM, MASSACHUSETTS

ABSTRACT

Metallurgical microstructure plays a major role, through its influence on magnetic flux pinning, on the critical current density of superconducting materials It has been found in technological practice that the capabilities of superconducting materials, as measured in short length samples, are rarely realized when long lengths of the same material are wound in a solenoid. This degradation has been attributed to magnetically induced thermal instabilities. A method is proposed for the preparation of stable superconducting cables comprising a filamentary phase of one superconducting in a matrix of another This is to be achieved by directional solidification of appropriate superconducting systems under 0 g conditions.

Metallurgical microstructure plays a major role, through its influence on magnetic flux pinning, on the critical current density of superconducting materials. It is the purpose of this paper to outline the reasons for this relationship and indicate how, by taking account of recent theoretical and experimental advances, carefully chosen eutectics

*Paper presented by J. T. A. Pollock

solidified under conditions of 0 g would have major advantages over materials presently available.

First, consider only ideal homogeneous superconducting materials. These may be easily separated into two groups by their transition from the superconducting to the normal state in an increasing external magnetic field, H_e (Fig. 1). As the applied magnetic field is increased, type I (soft) superconductors have an abrupt transition at a single critical field (H_c), while type II (hard) superconductors undergo a gradual transition to the normal state between a lower critical field, H_{c1}, and an upper critical field, H_{c2}. Thermodynamic relationships hold for both reversible processes, and the work done in driving the material normal is given by the area under the curves. For type II material, an imaginary thermodynamic critical field, H_c, may be defined by assuming an abrupt transition enclosing an equal area (dashed line in Fig. 1b). The degree of type II behavior may then be described by the dimensionless Ginzberg-Landau parameter, $\kappa = H_{c2}/\sqrt{2}\, H_c$. Theory indicates that κ depends primarily on the superconducting critical temperature, T_c, the electron density of states at the Fermi level, $N(0)$, and the normal state resistivity, ρ_n. κ is, therefore, sensitive to alloy concentration. Its relationship with the resistivity is given by the following equation:

$$\kappa = \kappa_0 + 7.5 \times 10^{-3}\ \gamma^{\frac{1}{2}}\ \rho_n$$

where κ_0 is the κ value for the pure element or compound, and γ is the coefficient of electronic specific heat. Thus, while elements (with the exception of Nb) are known to be type I, solid solutions, other than the very dilute, are type II. Intermetallic superconducting compounds are also type II, because their high $N(0)$ values result in a large κ_0. Table I gives values of T_c for metals, alloys, and compounds, together with H_c or H_{c2} (listed as H_n) values at 4.2 °K. It is apparent that high field superconducting materials must have type II characteristics, i.e., they must be either alloys or compounds.

Between H_{c1} and H_{c2}, type II materials are described as being in a "mixed state." To be useful for high field applications, a superconducting material must not only have a high H_{c2}, but must be able to carry large resistanceless currents in this mixed state. As the applied field is increased above H_{c1}, partial field penetration occurs in the form of quantized magnetic flux threads which consist of a normal core supported by a vortex of shielding current. This flux lattice, representing an internal magnetic field, B, has been directly observed,[3,4] and a balance is reached between the mutual repulsion of the fluxoids and the applied field force. If a current (J) is passed through the conductor at right angles to the direction of the applied field, a Lorentz force given by the cross product of $\vec{J}$ and $\vec{B}$ acts on the

flux threads in a direction perpendicular to both the applied field and the impressed current. In a homogeneous material, the flux lines will move and resistance will appear if the drift rate is sufficiently high. Thus, ideal reversible type II superconductors are expected to have low critical currents (Fig. 2).

If, however, the flux motion can be impeded by imperfections in the superconductor, the Lorentz forces may be resisted and the material can carry large superconducting currents without reverting to the normal state. Inhomogeneities [5,6] such as nonuniform dislocation arrangements, coherent precipitates, finely dispersed second phase, and voids can all aid in raising the critical transport current density, J_c. A flux line will remain "pinned" at an inhomogeneity until the Lorentz force exerted on it exceeds the pinning strength. When, as a result of increasing applied field or impressed current, the Lorentz force exceeds the value of the local pinning forces, a change in the flux line gradient will occur. If a balance with local pinning forces in another part of the superconductor does not take place, the superconductor will transform to the normal state and a resistance to current flow will be observed. The greater the differences in free energy of the inhomogeneity and the superconducting matrix, the greater its effectiveness in raising J_c (or, the greater the difference in electronic properties, the greater the pinning force).

This resistance to the motion of magnetic flux lines under the influence of the Lorentz forces will also result in an altered magnetization curve. The presence of heterogeneities causes a resistance to field penetration in increasing fields and impedes the flux thread escape in decreasing fields. This means that the magnetization curves for high field, high transport current superconductors are irreversible. Fig. 2 is a schematic representation of the way magnetization characteristics and critical current densities are altered by deviations from ideal behavior produced by inhomogeneities. Note that the magnetic hysteresis resulting from the nonhomogeneous nature of the material is a measure of the resistance to flux motion and, hence, of critical current densities in the mixed state. A quantitative theory relating J_c and magnetization data is available. [7,8]

Thus, the ultimate critical current densities which can be carried are controlled by interaction between the metallurgical microstructure of the sample and the magnetic flux thread lattice present in the mixed state.

In practice, it has been found that the capabilities of superconducting materials, as measured in short length samples, are rarely realized when the same material is used in a solenoid. This degradation has been attributed to magnetically induced thermal instabilities and may

be explained as follows. Increasing temperature (T) results in a parabolic decrease in the critical field and critical current of a superconductor for $T < T_c$. The relationship for H_c is given by the equation

$$H_c(t) = H_0 (1 - t^2)$$

where $t = T/T_c$ is the reduced temperature, and H_0 is the critical field at 0 °K. The fact that J_c usually decreases at a faster rate than H_c is generally ascribed to thermally activated flux creep past barriers.[9] Local variations in the movement of flux past the pinning sites (e. g. , due to mechanical shock) can result in a local rise in temperature. Since dJ_c/dT is negative, the local J_c value is decreased, allowing more flux motion for a given applied field, H_e, and creating more temperature rise, etc. This is commonly known as a flux jump and can result in a premature transition to normality. As a result of the heat generated, severe damage to the device may occur. This has been a major problem in superconducting solenoids and the reason for the incorporation of large volumes of high conductivity copper (a non-superconductor) in magnet design.

Some experimental results reported by Livingston[10] indicate a possible solution to this problem. It is known that the precipitation of Sn from supersaturated Pb-In-Sn solid solutions (which are superconducting above 4. 2 °K) results in flux pinning and magnetic hysteresis as shown in magnetization measurements made at 4. 2 °K (Fig. 3, curve A). However, magnetization curves taken at 2. 0 °K (Fig. 3, curve B) indicate that, although H_{c2} increased as expected, a decrease in magnetic hysteresis and, hence, the critical current density, were also reported. These results can be explained on the basis of the different flux pinning ability of the Sn particles at the temperatures at which the data were taken. Sn is superconducting at temperatures below 3. 7 °K. The Sn precipitates act as preferred flux pinning sites for the fluxoids at 2 °K because, although the Sn particles are superconducting at this temperature, their order parameter (a measure of the proportion of available electrons which are superconducting) is smaller than that for the higher superconducting transition temperature Pb-In-Sn matrix. However, as the temperature increases, the Sn particles become normal at a faster rate than the matrix, and are normal at 4. 2 °K. During the temperature rise, their flux pinning ability increases with respect to the matrix and increases substantially when the transformation to normality occurs. Therefore, although H_{c2} (controlled by the matrix) decreases with increasing temperature, the magnetic hysteresis and J_c characteristics increase. Briefly, this means that within the range of applied magnetic field indicated in Fig. 3, dJ_c/dT is positive over the temperature range ~2. 0 to 4. 2 °K. This is significant, since it offers a method of controlling those magnetic (i. e. ,

transport current) instabilities in which a negative dJ_c/dT plays such an important role.

An examination of the commercial superconducting materials presently available indicates that although high pinning characteristics have been achieved through highly disordered structures and the introduction of the heterogeneities in the form of second phase particles, no attempt has been made to achieve positive dJ_c/dT characteristics. The nonsuitability of superconducting elements as useful materials except in specialized instances, e. g. , Nb for ac conduction, has been previously noted. Superconducting solid solutions and compounds are, therefore, of primary interest. The introduction of a second superconducting phase as a source of pinning sites leads us to consider ternary phase systems, since an examination of phase equilibria between the components of possible superconducting solid solutions and intermetallic compounds points to few binary systems which present favorable phase relationships for achieving positive dJ_c/dT. The behavior at low temperatures of mixtures of superconducting phases is dependent not only on the electronic properties of the phases at these temperatures but also on their distribution and relative proportion. In particular, it is essential that the primary superconducting phase be present in electrically connected networks if resistanceless operation in high magnetic fields is to be realized. The need to meet this condition of multiple connectedness suggests that directional solidification of continuous fibers of the primary superconducting phase in a superconducting matrix of the second superconductor would be the ideal method for preparing a material with positive dJ_c/dT characteristics.

Directional solidification of binary eutectics has been used to prepare in situ intermetallic compound fibers in a metal matrix, and successful results have been reported in such systems as Cu_2Al in Al[11] and Al_3Ni in Ni[12]. Several problems are, however, encountered in such systems mainly associated with the invariant nature of a eutectic reaction. Normally, no adjustments in fiber-matrix ratio can be made and no influence on the properties of the matrix can be exerted. This latter factor is a severe shortcoming, since control of the matrix composition is essential in optimizing any alloy system. Nevertheless, composite electronic materials have been prepared by directional solidification of binary eutectics and show interesting properties which have made possible their use as polarizers for infrared light[13] and armatures for miniature electric motors.[14]

Since the use of ternary systems is envisioned in the preparation of the proposed superconducting materials, another class of phase reactions presents itself which leads to the same final structure as that of invariant binary eutectics, yet offers a means of overcoming some of

their shortcomings. The class of reactions proposed consists of monovariant eutectics present in higher order systems. The usefulness of these monovariant reactions arises from the fact that the crystallized binary eutectic type structure obtained is actually a solid solution matrix and a eutectic precipitate. The structure forms essentially in the same way as a binary eutectic by the simultaneous precipitation of two crystallite types, one of which is a solid solution and may consist of an essentially infinite number of alloying elements. Also, in certain cases and within limits, the fiber-matrix ratio may be variable. However, the most important possibility offered by the use of monovariant eutectics is that of controlling the matrix composition. This will allow relative adjustment in the superconducting properties of the phases, primarily T_c, to produce an essentially two-phase material with positive dJ_c/dT characteristics It has also been demonstrated[15] that control of the matrix composition can be a method of changing the crystallization behavior of the fibers.

It will be relevant to consider, briefly, the properties of eutectic composition material, paying particular attention to their preparation under directional solidification conditions. As pointed out previously, a eutectic structure, when directionally solidified, can consist of one rodlike or lamellar component of very high length-diameter ratio embedded in a matrix of the other eutectic component. Generally, however, as has been discussed by several authors,[16] small temperature fluctuations which cause convection and attendant changes in supersaturation cannot be avoided. Thus, fibrous growth of one component is interrupted; the filaments, instead of being continuous, become discontinuous. In other words, since the eutectic is an invariant point in the thermodynamic description of the system, for ideal eutectic solidification, temperature and composition are fixed. Local compositional variations such as those induced by convection cause a disruption of ideal thermodynamic growth conditions. As a consequence, fibers become irregular, or cells develop and a much less than ideal composite is the result.

In the case of monovariant eutectic reactions in higher order systems, these difficulties are sharply amplified because the liquid from which the fibers are precipitated contains more than two species of atoms, and the probability of producing local compositional gradients is consequently much greater. It is therefore suggested that directional solidification of superconducting monovariant eutectics would greatly benefit from the absence of gravity segregation and thermal convection, and that substantial advances in superconducting technology might be realized by manufacturing in space.

At present, there is a paucity of information available on ternary phase systems. It would, therefore, be necessary to investigate the phase

equilibria in systems which are tentatively suggested in order to determine whether suitable eutectic reactions are present. The superconducting characteristics of the materials can, however, be determined during the initial investigation and will themselves yield valuable phase equilibria information. Nevertheless, several interesting possibilities based on Nb compounds and solid solutions present themselves. Nb based A-15 type intermetallic compounds have the highest T_c measured to date [$Nb_3(Al_{0.8}Ge_{0.2})$, $T_c = 20.05$ °K)]. We suggest that suitable monovariant eutectic reactions may be found among such ternary systems as Nb_3Al, Nb_3Ge, Nb_3Sn with V, Ti, Ta, etc. These ternary systems would allow, if successful, the directional solidification of a high T_c intermetallic compound in an Nb based solid solution which would, on the basis of information available,[17, 18, 19] also have a high T_c and excellent J_c characteristics.

Initially, feasibility experiments could be carried out by producing directionally solidified eutectics with the correct current density characteristics in a Pb based ternary material. Pb based compounds and alloys have superconducting transition temperatures well above 4.2 °K (boiling point of liquid He) and, because of their low melting points, the additional advantage of easy preparation. Also, there is some information on directional solidification of Pb alloys already available.[20] Meanwhile, phase diagram information could be generated in the more important transition metal systems which would have superior superconducting characteristics.

In summary, we have proposed a method of preparing superconducting material which would be stable in the presence of the flux jumps which can lead to a catastrophic transition to normality. The idea is based on three interconnected propositions:

1. The material should be multiphase. At least two phases should be superconducting and with electronic properties such that stability to flux jumps is possible.

2. To ensure continuity of the high current density superconducting path, directional solidification of eutectics under conditions of 0 g should be used to prepare the samples.

3. The use of multicomponent monovariant eutectic systems presents major advantages over invariant eutectics which have been successfully used to prepare composite materials. In particular, the ability to adjust the matrix composition is a tremendous advantage, since it allows proposition (1) to be more readily realized.

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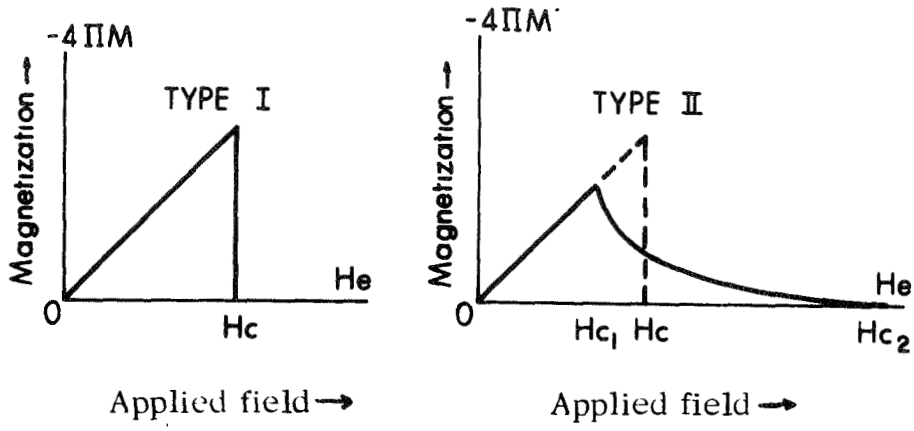

Fig. 1. Schematic magnetization curves for types I and II superconductors

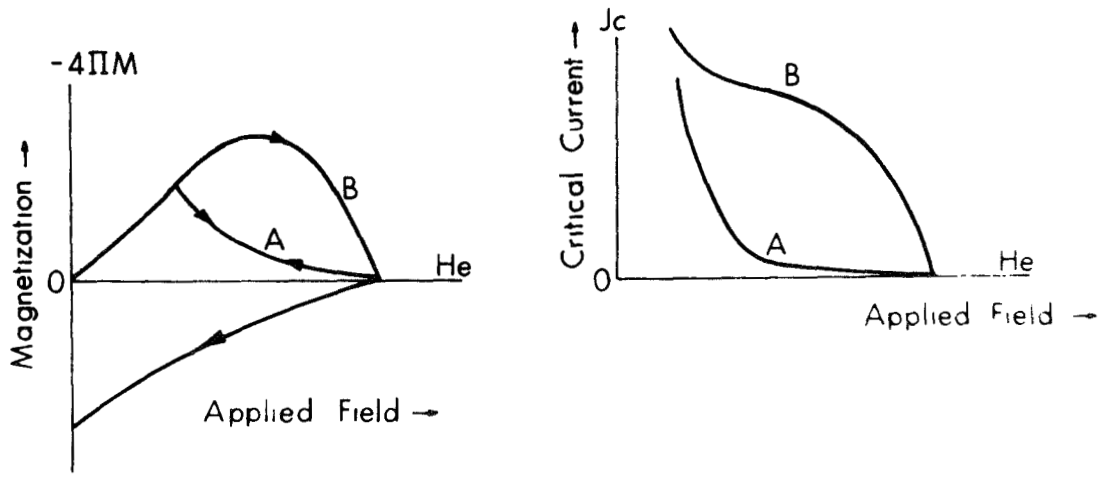

Fig. 2. Schematic magnetization and critical current density curves for type II superconductors (curve A = reversible magnetization curve and corresponding J_c curve; curve B = same material in, for example, a highly deformed condition — magnetic hysteresis is evident and a corresponding enhancement of J_c has occurred)

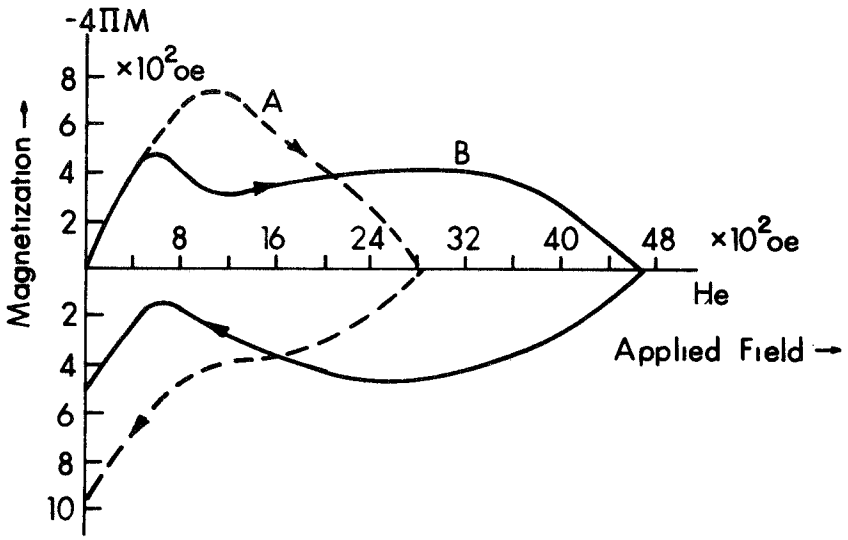

Fig. 3. Magnetization curves[10] for a Pb-22 a/o In-21 a/o Sn alloy aged 1 hr at room temperature after solution treatment (curve A = measurement at 4.2 °K; curve B = measurement at 2 °K)

Table I. T_c and H_n Values[1, 2]

Element	T_c, °K	H_n (oe)
Al	1.18	99
Nb	9.13	1980
Pb	7.20	803
Sn	3.72	309
Ta	4.48	830
V	5.30	1020
Alloys		K (oe)
Nb-25a/o Zr	10.8	~100*
Nb-33a/o Ti	9.3	~100*
Ta-35 → 100 a/o Ti	4.4 — 7.8	14-138+
Mo-33 a/o Re	10.8	~28+
Compounds		
Nb_3Sn	18.05	350+
Nb_3Al	17.0	
V_3Si	17.0	300+
PbBi (ϵ phase)	8.8	~30‡

*Extrapolated linearly to 0 °K.

+Measured at 1.2 °K.

‡Measured at 1.9 °K.